

PATENT SPECIFICATION

DRAWINGS ATTACHED

858,127



Date of Application and filing Complete Specification: June 7, 1957.

No. 18164/57.

Application made in United States of America on June 15, 1956.

Application made in United States of America on April 26, 1957.

Complete Specification Published: Jan. 4, 1961.

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International Classification:—B29b. C08g.

COMPLETE SPECIFICATION

Polymer Foam Modification

We, SCOTT PAPER COMPANY, a corporation organised under the laws of the State of Pennsylvania, United States of America, of Chester, State of Pennsylvania, United States 5 of America, do hereby declare the invention, for which we pray that a patent may be

use has been made of these structures as household and industrial sponges, chamois-like cleansers, and other articles where utility depends upon softness, hydrophilicity and porosity. 50

PATENTS ACT, 1949

SPECIFICATION NO. 858,127

In accordance with the Decision of the Superintending Examiner, acting for the Comptroller-General, dated the 20th day of May, 1964 this Specification has been amended under Section 14 in the following manner:-

Page 16, at the bottom of second column, delete the reference to Section 8 substitute

"Reference has been directed, in pursuance of Section 9, subsection (1) of the Patents Act, 1949, to Patent No. 789,481"

THE PATENT OFFICE,
12th August, 1964.

D 18667/1(7) /R.109 200 7/64 PL

whereby foamed open-cell, cellular structures 30 may be produced, as by the use of blowing agents and similar techniques for the incorporation of expanding bubbles of gas or vapour in a plastic mass of polymer, are fully described in published literature.

Such foamed polymeric products generally possess moderate tear-strengths and varying 35 degrees of softness and porosity depending upon the basic polymers utilized as well as the particular procedures employed in their cellulation. These products are resistant to many chemicals and bacterial action, and can be prepared in a wide variety of shapes, sizes and colours. However, while these products are frequently described in the literature as sponge-like, with reference to their cellular structure, they are usually of a hydrophobic character, failing to imbibe and hold water in the same 40 fashion as a natural sponge. Hence only limited

It is a principal object of the present invention to provide an integrally formed, permeable polymeric polyurethane structure of improved porosity and modified physical properties based upon a polymer including in 75

its linear chain connecting >C-C=O ,
 --O-C-N- , >C-C=O-N- , and/or
 >N-C-N- bonds or linking groups. 80

Another object of my invention is to provide a simple method of connecting hydrophobic open-cell, cellular structures of foamed polymer including in its linear chain connecting >C-C=O , --O-C-N- ,
 >C-C=O-N- , and/or >N-C-N- bonds 85 or linking groups into sponge-like products

[.]

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We, SCOTT PAPER COMPANY, a corporation organised under the laws of the State of Pennsylvania, United States of America, of Chester, State of Pennsylvania, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The present invention relates to novel open-cell, cellular structures including integrally formed, 3-dimensionally reticulated and spongiform products, and to the preparation thereof. More particularly the invention relates to foamed polymeric polyurethane materials which have been modified by treatment subsequent to their formation to impart thereto improved physical properties, including softness, hydrophilicity and capillaractive effect toward water, porosity and increased strength. Open-celled, cellular structures of foamed thermoplastic or thermosetting polymers are well known. Such cellular structures are sometimes referred to as low density foams, since they contain a minimal weight of polymer for the volume occupied by the mass. Methods whereby foamed open-cell, cellular structures may be produced, as by the use of blowing agents and similar techniques for the incorporation of expanding bubbles of gas or vapour in a plastic mass of polymer, are fully described in published literature.

Such foamed polymeric products generally possess moderate tear-strengths and varying degrees of softness and porosity depending upon the basic polymers utilized as well as the particular procedures employed in their cellulation. These products are resistant to many chemicals and bacterial action, and can be prepared in a wide variety of shapes, sizes and colours. However, while these products are frequently described in the literature as sponge-like, with reference to their cellular structure, they are usually of a hydrophobic character, failing to imbibe and hold water in the same fashion as a natural sponge. Hence only limited

use has been made of these structures as household and industrial sponges, chamois-like cleansers, and other articles where utility depends upon softness, hydrophilicity and porosity. 50

There are, of course, available on the market various types of sponge-like materials, for example, cellulated rubbers, regenerated cellulose sponge, partially formalized polyvinyl alcohol sponges which serve to supplement the supply of natural sponges. None of these commercial sponges, however, is free from certain disadvantages which seriously limits its field of application. Rubber sponges are comparatively hydrophobic, are subject to ageing, attack by ozone, and have relatively poor strength; regenerated cellulose sponges, while capable of imbibing and holding water, are stiff when dry and are readily subject to bacterial attack resulting in rapid disintegration upon use, partially formalized polyvinyl alcohol sponges are board-like and rigid when dry and have limited resistance to chemicals; natural sponges are expensive, are subject to chemical and bacterial attack, while their size, shape and texture are limited. 55 60 65 70

It is a principal object of the present invention to provide an integrally formed, permeable polymeric polyurethane structure of improved porosity and modified physical properties based upon a polymer including in

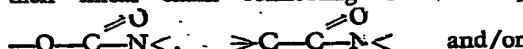
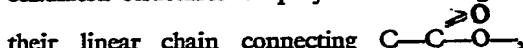
its linear chain connecting $>\text{C}-\text{C}=\text{O}$,
 $-\text{O}-\text{C}=\text{O}-\text{N}<$, $>\text{C}-\text{C}=\text{O}-\text{N}$, and/or
 $>\text{N}-\text{C}-\text{N}<$ bonds or linking groups. 75

Another object of my invention is to provide a simple method of connecting hydrophobic open-cell, cellular structures of foamed polymer including in its linear chain connecting $>\text{C}-\text{C}=\text{O}$, $-\text{O}-\text{C}=\text{O}-\text{N}<$,
 $>\text{C}-\text{C}=\text{O}-\text{N}<$, and/or $>\text{N}-\text{C}-\text{N}<$ bonds or linking groups into sponge-like products 80 85

possessing increased softness, hydrophilicity and capillaractive effect toward water.

Another object of the invention is to convert polymeric cellular structures to permeable low density materials of improved tear strength and exhibiting improved resistance to degradation on ageing under conditions of high humidity.

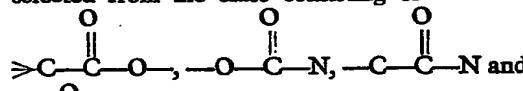
A further object of my invention is to provide a method of converting open-cell cellulated structures of polymers including in



3-dimensionally reticulated or skeletal structures in which a varying percentage of the cell faces initially present have been eliminated.

Other objects and advantages of the invention will be readily apparent from the following detailed description of various embodiments thereof.

In accordance with this invention there is provided a foamed, open-cell, cellular polymeric polyurethane material of the form of an integrally formed 3-dimensionally reticulated structure comprising a network of strands defining the outline of a plurality of polygons making up a plurality of polyhedrons, at least a major portion of the faces of the polyhedrons being open, in which at least a portion of the linking groups in the polymer chain are selected from the class consisting of



hydrolyzed.

It is believed that the polymeric product, after treatment, includes the original polymer having interspersed therein, either topically or topically and permutooidally, carboxyl and hydroxyl groups. This treatment alters either one or both of softness and hydrophilicity to an extent depending upon the degree of hydrolysis generally, and whether hydrolysis takes place internally of the polymer as well as on the surfaces and the degree to which the surfaces of the polymer have been hydrolytically attacked. Hence, depending upon the exact conditions followed, the improvement may be predominately in (a) softness, or in (b) hydrophilicity and increased capillaractive effect towards water, or toward (c) increased hydrophilicity and capillaractivity and decreased density, or toward (d) increased softness and decreased density, or toward (e) increased softness, hydrophilicity and capillaractivity and decreased density. The properties of the resulting product will also depend somewhat on the pore size of the starting material, this

determining the pore size or the skeletal framework of the end product.

The presently provided highly porous integrally formed 3-dimensional network structures in which the polymer strands have been formed by a foaming or blowing procedure possess a unique and highly advantageous construction in which the polymer strands intersect in a non-planar configuration, and are of outstanding strength and cohesiveness. In the modification of the process of this invention, wherein the treatment with a hydrolyzing agent is continued until at least a major portion of the cell faces are eliminated, and there is recovered a reticulated structure, foamed open-cell cellular structures comprising polymer in which at least a portion of the bonds

of the polymer chain are $>\text{C}(=\text{O})-\text{C}-\text{O}$,

$\text{O}-\text{C}(=\text{O})-\text{N}<$, $>\text{C}(=\text{O})-\text{C}-\text{N}<$, and/or

$>\text{N}-\text{C}(=\text{O})-\text{N}<$, bonds are converted into structures of decreased density and greatly increased porosity. Additionally, it has been found that the products obtained by this process may be improved, as compared to the cellular structures from which they are obtained, in the qualities of softness and compliance, tear strength, tensile strength at unit density, and/or resistance to degradation of load-bearing properties on ageing under conditions of high humidity; furthermore, reticulated structures prepared in accordance with this invention from polymeric polyurethane open-cell cellular structures may have imparted thereto the quality of hydrophilicity.

The compression/deflection characteristics of flexible cellular structures converted to porous reticulated products by the present process are altered and improved for certain applications. The particular properties of the 3-dimensional network structures obtained vary, depending on the nature of the polymer comprising the strands of which they are constructed, and on the size and spacing of the strands; and the products range from soft, lacy, diaphanous materials to stiff and harsh porous structures. Flexible and soft network structures prepared in accordance with this invention are of particular interest, in the form of thin sheets, as materials for use in the construction of insulating linings for coats, jackets, and similar garments, since the present materials of high tensile strength are strong and readily sewn, and are substantially free of difficulties with tearing and shredding encountered with previously known polymeric foamed cellular structures. For such application in the manufacture of clothing, and the like, the hydrophilic character of the polymeric polyurethane structures is of particular advantage. Additionally, depending on the nature and properties of the reticulated products, such as pore size and flexibility, the novel materials pro-

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vided by this invention are of utility as filtering devices, gas-liquid contacting devices, catalyst carriers, rug anchors, door mats, drain pads, scouring pads, sponges, insulating pads, tire liners, spacing devices, flexible partitions, draperies, upholstering padding, mattresses, and pillows.

The present invention will be more readily understood from a consideration of the drawings, in which:

Figure 1 is a perspective view of a block of a foamed open-cell cellular structure of a polymer in which at least a portion of the bonds of the polymer chain are $>C-C=O$,
 15 $-O-C(=O)-N<$, $>C-C(=O)-N<$, and/or
 $>N-C(=O)-N<$, bonds;

Figure 2 is an enlarged view of the surface of the block of Figure 1 within area 2; wherein may be seen strands 3 and membranes 4 of polymer defining cell edges and faces;

Figure 3 is an enlarged view of the same area as in Figure 2, after treatment in accordance with one embodiment of the invention, whereby at least a major portion and preferably substantially all the cell faces are removed, leaving a 3-dimensional networks of strands;

Figure 4 is an enlarged perspective view of a typical cell of the block in Figure 1;

Figure 5 is a sectional view taken along line 5-5 of Figure 2;

Figure 6 is a sectional view taken along line 6-6 of Figure 3; after the cellular structure has been subjected to treatment in accordance with one embodiment of the invention;

Figure 7 is an enlarged perspective view of a typical cell of the block in Figure 3; and

Figure 8 is an enlarged view of the nexus of the strands in the cell illustrated in Figure 7, within area 6.

In the preparation of foamed polymeric polyurethane cellular structures, as gas or vapour is generated while the material to be formed is in the plastic state. The generation of this gas results in the formation of bubbles, approximately spherical in form. As these bubbles expand, cells are formed which have more or less definite geometric configurations. The optimum packing for spheres is an arrangement in which each sphere is surrounded by 12 other spheres; and correspondingly it has been found that the cells formed by the expansion of gas bubbles to the point of contact, so as to produce low-density, open-cell cellular structures, generally are in the form of dodecahedrons, with pentagonal sides or faces. This is the general rule, though in any foamed mass will be found cells of varying geometry. At the intersection of the faces there are relatively heavy strands of material, and between the strands, the actual faces or cell walls are very thin membrane-like films. One

or more, but generally a minor proportion of the faces of the cells are ruptured during foaming, so that in the mass the cells are interconnected and hence the mass is referred to as open-celled. The foregoing is illustrated in Figure 4, which illustrates, enlarged, a typical cell; 4 represents the thin, membrane-like cell face, and the relatively heavy strands at the junctions of the faces are represented by 3.

According to the present invention, the foamed mass of polymer is exposed to the action of a hydrolyzing agent under hydrolyzing conditions. Under one embodiment of the invention, the hydrolysis is so controlled as to alter the physical characteristics of the strands and faces of the foamed polymer without, however, attacking the cell faces sufficiently to remove all that exist in the untreated mass. On the other hand, hydrolysis conditions and the extent of hydrolysis may be so selected as to remove substantially all of the cell faces leaving only a skeletal structure made up of the interconnected strands.

The polymer comprising presently useful cellular structures is characterized by bonds

selected from $>C-C=O$, $-O-C(=O)-N<$,

$>C-C(=O)-N<$ and $>N-C(=O)-N<$ comprising

at least a portion of the bonds of the polymer chain. By bonds of the polymer chain are meant bonds connecting recurring chain units in polymeric molecules, and forming the binding forces whereby the polymeric nature of the molecule is maintained. These bonds may be interspersed between radicals containing only a few carbon atoms each, the repeated bond and radical units in totality forming a polymer; or the bonds may connect molecular chains which are individually polymeric in nature, the bonds having either a chain-extending or a cross-linking relationship to these polymeric molecular chains. As opposed to functional groups dependent from polymeric molecules, bonds of the polymer chain, at least at positions removed from the chain ends, are molecular-weight controlling; on cleavage of a single such bond, the polymer molecular weight is decreased substantially.

Polymers of this type are generally condensation polymers, but are not limited thereto.

Condensation polymers in which the polymer

chain includes $>C-C=O$, $>N-C(=O)-N<$,

and/or $>C-C(=O)-N<$ bonds comprise poly-

esteramides, polyamides, urea-formaldehyde resins and the like. Polyesteramides contain

both $>C-C=O$ and $>C-C(=O)-N<$ bonds

in the polymer chain, and each of these bonds is susceptible to cleavage by hydrolyzing agents.

Polyesteramides are prepared, for example, by reaction of a polyfunctional acid

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- with a polyfunctional alcohol and a polyfunctional amine, whereby some of the acid groups bond with the alcohol to form ester linkages, and some with the amine to form amide bonds. Polymers containing both amide and ester bonds can also be produced by adding an amino acid to the components of a polyester, as is known in the art. In generally similar fashion to the polyesteramides, the units from which a polyamide chain is built up may be heterogeneous—an acid and an amine—or homogeneous—either amino acids, as in proteins, or products of opening up lactam rings. The urea-formaldehyde resins
- 15 contain $>N-C=\overset{\text{O}}{N}<$ groups; they are prepared by condensation of urea and formaldehyde, optionally with addition of one or more modifiers, which may, for example, be alcohols or the like.
- 20 Another and particularly preferred class of polymers which, in the form of cellular structures, are modified in accordance with this invention, comprises isocyanate-modified polymers. The isocyanate-modified polymers are polymeric materials wherein residues of polyisocyanate, such as toluenediisocyanate, form a part of the polymer chain.
- The type of bond into which the isocyanate radical is converted in the chain-forming reaction may be a urethane bond, $-O-C=\overset{\text{O}}{N}<$,
- 30 a urea bond, $>N-C=\overset{\text{O}}{N}<$, and amide bond $\overset{\text{O}}{C}-C-N<$, or other, depending on the functional group or compound with which the isocyanate radical has reacted. In general the polyisocyanate residues form only a minor portion of the chain in isocyanate-modified polymers; the polyisocyanates act as chain extenders for other polymeric molecules furnishing functional groups with which isocyanate radicals react, and link these polymeric molecules together into composite ultimate polymer molecules. The initial polymeric molecules with which the polyisocyanate is reacted may be designated secondary polymers.
- Isocyanate-derived polymers are particularly readily prepared in the form of foamed, open-cell cellular structures, since the gas by which the polymer is foamed may be generated by the same reactions by which bonds in the ultimate polymer chain are formed. One class of secondary polymers from which foamed isocyanate-derived polymers may be produced comprises polyesters, as described hereinabove.
- 55 If, in the synthesis of the polyester, the polyfunctional acid is present somewhat in excess as compared to the polyfunctional alcohol, the resulting polyester contains terminal free acid groups. Reaction of isocyanate radicals with such carboxylic acid groups results in formation of amide bonds, with generation of foam-

forming carbon dioxide as a byproduct; by virtue of their polyfunctionality, the polyisocyanate residues function as bridges between the molecules of the polyester chains, and produce cross-linked high molecular weight polymers.

65 Alcohol-terminated polyesters are also convertible to isocyanate-derived polymers, and hydroxyl-substituted polymers or polyols, such as polyesters containing free hydroxyl groups, are the secondary polymers used to prepare an important class of isocyanate-derived polymers, the polyurethanes. The reaction by which isocyanate-derived polymers of the polyurethane type are prepared, involving the union of a hydroxy group with an isocyanate radical to form a urethane bond, is not productive of byproduct carbon dioxide, in contrast to the amide-forming condensation reaction described above. For foam production, an isocyanate-derived polymer of the polyurethane type may be treated, during or subsequent to reaction of the polyisocyanate with the secondary polymer or polyol, with a chain extending agent, usually water, with which isocyanate radicals react to form carbon dioxide, while urea bonds $-NHCONH-$, are generated.

70 Isocyanate-derived polymers prepared by reaction of a polyisocyanate with a polyol are described by reference to the nature of the bond formed by the isocyanate radical in reaction with the secondary polymer, and by the nature of the secondary polymer. Thus, the isocyanate-derived polymers prepared by reaction of a polyisocyanate with a polyol of the polyester type are designated polyester polyurethane polymers or polymeric polyester polyurethanes; if desired, they may more briefly be referred to as polyester polyurethanes.

75 Open-cell foamed cellular structures of polymeric polyester polyurethane form one particularly preferred starting material for preparation of modified structures in accordance with this invention. Any of a variety of polyesters may be employed in preparation of such cellular structures. It is possible to prepare isocyanate-derived polymers from monomeric polyol polyesters of relatively high molecular weight, such as castor oil. Preferably, the present polyurethanes are prepared from polymeric polyesters, as described hereinabove. These polyesters may comprise simple straight-chain polymers such as the reaction product of adipic acid and diethylene glycol, or may be styrene- or oil-modified or otherwise varied, as is well understood in the art of foamed isocyanate polymer synthesis. As will be apparent from the description above of the chemical bonds involved in the steps of isocyanate-derived polymer foamed cellular structure synthesis, in foamed isocyanate-derived polymers prepared on a basis of a polyester secondary polymer, whether the

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polyester is a polyol, that is, a polymer containing hydroxy groups reactive with isocyanate radicals, whether the reactive functional groups of the polyester are acid radicals, the foamed cellular structure obtained will contain ester hydrolyzable bonds and also urethane, amide, and/or urea hydrolyzable bonds; and one or more of the hydrolyzable types of bonds present in the polymer may be attacked in preparation of modified structures by treatment of the foamed cellular structure in accordance with this invention.

Another class of polyols with which polyisocyanates may be reacted to form foamed open-cell cellular structures comprises polyethers, and the modification of such cellular structures forms another preferred embodiment of this invention. Illustrative of polyethers from which foamed cellular structures of polymeric polyether polyurethanes may be prepared are aliphatic alkylene glycol polymers, as exemplified by poly-1, 4-butylene ether glycol. Aliphatic ether bonds are generally resistant to hydrolysis, but the urethane and urea bonds in polyether polyurethane foamed products are susceptible to hydrolytic cleavage, and it is believed that hydrolysis of the urethane and/or urea bonds is involved when polymeric polyether polyurethane cellular structures are converted by hydrolyzing agents in accordance with this invention to yield modified structures. Additionally, polyether molecules may include the residues of a variety of compounds such as amines and the like, which are reactive with alkylene oxides, from which latter compounds polyethers are prepared. Such polyethers may also be used for preparation of polymeric polyurethane cellular structures, and foamed products of this type may be susceptible to hydrolytic attack not only at urethane and urea bonds,

but also at $\text{C}-\text{C}-\text{N}$ bonds and similar chain linking bonds, especially tertiary amine positions, sensitive to hydrolysis. In another variation, a polyether may be modified by reaction with an epoxy resin prior to or concurrently with introduction of isocyanate residues and production of a foamed cellular product. Procedural details and variations which may be made in selection of the nature of the polyether used, the polyisocyanate with which it is reacted, and so forth, are well known in the art.

In further extension of the scope and variety of isocyanate-derived polymer foamed cellular structures available, polyisocyanates may be reacted under foam-producing conditions with any of a number of different polymers wherein functional groups reactive with isocyanate radicals are present, including polyesteramides and alcohol-modified urea-formaldehyde resins.

The pore size of cellular structures produced in isocyanate-derived polymer synthesis may

be controlled as desired, by adding foam-stabilizing or coalescing agents. The flexibility of the products may be varied by judicious selection of secondary polymer and isocyanate with respect to chain branching, steric hindrance of rotation and similar considerations.

The production of foamed open-cell cellular structures of isocyanate-derived polymers of various types is well understood in the polymer art, and is described for example in "German Plastics Practice", published by Debelle and Richardson, 1946, Chapter 21, "Plastic Foams", pages 462-465; in "Papers Presented at the Atlantic City Meeting: Synthesis of Isocyanate Polymers" published by the American Chemical Society, Division of Paints, Plastics and Printing Ink Chemistry, September, 1956; and in the patent literature.

To modify low density open-cell cellular structures comprising polymer in which at least a portion of the bonds of the polymer

chain are >C-C=O , --O-C=O-- , >C-C=N< , and/or >N-C=N< bonds

in accordance with this invention, the cellular structures are exposed to the action of a hydrolyzing agent under hydrolyzing conditions. By a hydrolyzing agent and hydrolyzing conditions are here meant agents and conditions productive of hydrolysis. The bonds present in these polymeric materials are susceptible of hydrolysis, and it is believed that at least one of the effects involved in the present process is hydrolysis of a portion of the bonds identified as constituting linking groups within the polymer chain. Hydrolysis is defined as a decomposition reaction caused by water. Water alone may be used as the hydrolyzing agent in the present process if the temperature is elevated sufficiently to induce the hydrolysis reaction; and/or the hydrolysis may be catalyzed by hydroxyl ions, by hydrogen ions, or by enzymes. In accordance with the present process, these factors of temperature and the presence or absence and concentration of catalyst are controlled, together with time of treatment, while cellular structures are exposed under hydrolyzing conditions to alter their physical properties to the degree desired.

The hydrolysis is purposely controlled in order that the skeletal celliform structure of the mass, that is, the outline of the cellular structure is not destroyed, as can readily be determined by visual inspection. There is a wide range of latitude in the extent of hydrolysis which may be allowed to occur, from a slight surface modification of the cell surfaces merely to improve softness or hydrophilicity to scant removal of a major portion of the cell faces, with a marked increase in porosity of structure, and continuation of hydrolysis until the strands are attacked to

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- some extent, and thinned down, with a consequent substantial softening of the structure. Properties such as softness and porosity generally increase proportionately to extent of hydrolysis, while strength properties may pass through a maximum and subsequently decrease; the severity of the hydrolyzing conditions may accordingly be varied depending on the qualities desired in the product. Weight loss paralleling the progress of the hydrolysis, the degree of which varies with the nature of the polymer, may be useful as a measure of the extent of hydrolysis occurring and change in properties of the structure being produced by the treatment. For example, for polyester polyurethanes, a weight loss of about 5-15%, preferably about 10%, appears to give optimum strength properties.
- Since water is the hydrolysis reactant, the hydrolysis in accordance with the present invention will be carried out in the presence of water, either alone, in which case it is employed at a high temperature, or in the presence of a catalyst. When water alone is employed, it is preferably utilized at temperatures ranging from about 100°C. up to the softening point of the polymer. Thus, for example, in this embodiment, steam, superheated steam or heated water under superatmospheric pressures may be employed. Advantageously, hydrolysis catalysts are employed together with water in the treatment. It is possible to use enzyme hydrolysis catalysts including an esterase such as lipase, a protease such as pepsin, and so forth. Preferred are ionic catalysts, which may be acids supplying hydrogen ions or bases supplying hydroxyl ions in aqueous solution.
- Particularly efficacious as hydrolyzing agents in the process are hydroxyl ions, as supplied by aqueous alkali, dilute or concentrated. The alkaline material may be any of the common bases providing the desired hydroxyl ions, such as the alkali hydroxides, like sodium hydroxide or potassium hydroxide; ammonium hydroxide; quaternary ammonium bases such as benzyltrimethylammonium hydroxide; amines such as methylamine; and alkaline salts such as trisodium phosphate.
- When aqueous alkali is employed, lower temperatures can be used than with water alone or steam, depending on the rate of hydrolysis desired and the alkalinity of the solution; and in most cases desired result can be obtained at temperatures between about 20°C. and the boiling point of the solution at atmospheric pressure, although higher temperatures, as discussed above, can be used. When aqueous alkali is employed, particularly advantageous results are obtained when the pH of the medium is above about 8.5, and preferably above about 10.
- Alternatively, the hydrolysis may be carried out in the presence of aqueous acid, either dilute or concentrated. Exemplary of inorganic

acids that may be employed are hydrochloric acid, sulphuric acid, and phosphoric acid. Examples of organic acids that may be employed are sulphonic acids such as toluene sulphonic acid, and carboxylic acids such as acetic acid. When aqueous acid is employed, particularly advantageous results are obtained when the pH of the medium is below about 5.5, preferably below about 4. The temperature of the solution may be as described above in connection with alkaline solutions.

The process of the present invention may also be carried out in successive stages; for example, a polymer mass may be treated with steam at high temperatures to soften the structure without rupturing the cell faces, and thereafter treated with aqueous sodium hydroxide to produce the reticulated structure of the invention.

Referring further to the drawing, a block 1 comprises an open-celled cellular polymer in which at least a portion of the bonds

of the polymer chain are $\text{>} \text{C}=\text{C}-\text{O}$,

$\text{--O}-\text{C}=\text{O}$, $\text{>} \text{C}=\text{C}-\text{N}<$ and/or

$\text{>} \text{N}-\text{C}=\text{O}$ bonds or linking groups.

Within a representative area 2 there will be visible a plurality of strands 3 forming junctions between cell faces 4 or cell walls which are thin, membrane-like films of polymer material. During cellulation of the polymer, certain of the cell faces 4 will rupture producing open areas 5 to establish intercommunication between adjacent cells. Mild hydrolysis of the foamed polymeric mass illustrated in Figures 1 and 2 so modifies the polymer surfaces that the polymer mass changes from hydrophobic to hydrophilic although there is no visible change in the mass per se.

Additional hydrolysis effects the removal of a major portion and preferably substantially all of the cell faces 4 and the remaining reticulated structure, as seen in Figures 3 and 7, is essentially a 3-dimensional network of strands 3a defining the outline of the original cell faces and surrounding the open areas 5.

A strand nexus 6 is shown in an enlarged view in Figure 8, which illustrates clearly the triangular nature of the polymer strands at the points of intersection as well as the non-planar nature of the nexus 6. It will be observed that the nexus of the strands is thickened as compared to the strands per se; consequently, in the reticulated structure derived from the initial cellular product, the intersections of the strands are particularly strong and coherent. Each strand 3a diverges from the other three strands at the nexus 6 at an angle approximately normal to the plane of the other three strands, and, as a result, the resulting reticulated structure tends to be isotropic and non-directional in response to

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stress.

In the original cellular structure, the strands are roughly triangular in cross-section; when cell faces are removed during hydrolysis, the angular nature of the strands may be retained, or following more extensive hydrolysis, the strands may be thinned down and rounded off.

The average diameter of the polygonal cell faces outlined by the strands 3 and 3a may vary, as determined by the pore size or cell-face diameter of the original cellular structures or from about 0.05 mm to about 20 mm. Foam forming techniques are sufficiently developed to enable close and accurate control of pore size and uniformity of product.

Examples 2 to 4, 6 to 11, and 15 to 20 illustrate the present invention, but are not intended to limit the scope of the invention in any way. Examples 1, 5, 12 and 14 illustrate preparations of starting materials.

EXAMPLE 1.

This example describes preparation of a polymeric polyester polyurethane.

Component A.

Into a closed container equipped with an agitator and means for maintaining a nitrogen gas sweep are charged, at room temperature, 50 parts by weight of an approximately 80:20 isomeric mixture of toluene-2,4-diisocyanate and toluene-2,6-diisocyanate, (sold under the registered Trade Mark "Hylene" TM by E. I. du Pont de Nemours & Co., Inc., Wilmington, Delaware), and 50 parts by weight of a polyester resin (alkyd) (sold under the registered Trade Mark "Paraplex U-148" by Rohm and Haas Company, Philadelphia, Pa.), having the following properties:

number average molecular weight	1800—2000
equivalent weight	745—830
hydroxyl number	65—75
acid number	3 maximum
water content	0.25% maximum
average hydroxyls per molecule	2.42

The above-described mixture is agitated under a maintained nitrogen atmosphere for four hours, the temperature rising to approximately 32°C.

Component B.

There are blended at room temperature: 80 parts by weight of the polyester resin referred to above, 0.6 parts by weight of a polyoxyethylated vegetable oil dispersing agent (sold

under the registered Trade Mark "Emulphor" EL-719 by General Aniline and Film Corp., New York City, N.Y.), 4.5 parts by weight of water and 1.9 parts by weight of diethyl-ethanolamine.

100 parts by weight of component A are added to 87 parts by weight of component B, and thoroughly mixed for about 20 seconds at a starting temperature of about 25°C. The mixture is then immediately poured into a container of sufficient volume to permit expansion. After about 15 minutes the product sets to a cellular mass, the temperature rising to about 75°C. The container together with the foamed cellular mass is placed in an oven and held at 70°C. for approximately 16 hours. The product, in the form of an open-cell, foamed mass and having carboxylic ester linkages, is removed from the container and cut into blocks.

The blocks have a density of 0.046 grams per cubic centimetre. The proportion of closed cells in the product is very small, and the cell faces have an approximate diameter of 0.3 mm.

EXAMPLE 2.

This example describes preparation of a reticulated polyester polyurethane structure.

Blocks of open-celled polyester polyurethane cellular product 12.5 x 7.5 x 2.5 cms. prepared as described in Example 1 and having a tensile strength of 28.5 pounds per square inch (2.0 kilograms per square centimetre) are immersed for various periods of time in a bath at a temperature of 50°C. composed of:

Sodium hydroxide ... 100 parts by weight	90
Water 900 parts by weight	

The blocks are repeatedly kneaded in the bath to ensure thorough penetration of the solution. The blocks are then removed from the bath, washed thoroughly with cold water, and immersed in a 2% aqueous acetic acid solution and repeatedly kneaded therein to neutralize any remaining sodium hydroxide, then washed with water. The blocks are then placed in an oven held at 120°C. and held there for 2 hours. This treatment after 10 minutes, results in removal of cell faces leaving a fine network of the original strands defining the outlines of the original cells. After 20 minutes treatment, the reticulated structure is retained, but a light, softer product is recovered. The effect of treatment is as follows:

Time of Treatment (minutes)	Softness (mm.)		Hydrophilicity (%)	Density (grams per cc.)	Weight Loss (%)
	Dry	Wet			
0	5	9	12	0.046	0.0
2	8	10	27	0.044	3.5
5	8	11	87	0.0438	4.2
10	9	12	89	0.0414	10.9
20	15	20	89	0.0319	30.5

Softness is measured by the penetration of a 12.7 mm. diameter steel hemisphere under a total load of 300 grams.

- Hydrophilicity is measured herein as follows: a block of the cellular mass to be tested (of a size 12.5 x 7.5 x 2.5 cms.) is squeezed several times under water. The block is withdrawn and excess water is removed by manually squeezing, and the weight of the wet squeezed block is noted. 30 ml. of water are poured on to a flat sheet of polystyrene to make a puddle. The block is gently placed on the puddle, large face down, for a period of five seconds. The block is again weighed. The amount of water absorbed is calculated and recorded as per cent of the original 30 ml.

EXAMPLE 3.
In this example blocks prepared as in

Time of Treatment (minutes)	Softness (mm.)		Hydrophilicity (%)	Weight Loss (%)
	Dry	Wet		
0.0	5	9	12	0.0
0.5	6	9	12	0.0
1.0	8	12	13	1.0
2.0	10	14	16	2.9
4.0	13	20	18	6.0

EXAMPLE 4.

This example describes preparation of another reticulated polyester polyurethane structure.

A foamed open-celled polyester polyurethane cellular structure prepared as described in Example 1 was cut into blocks 12.5 x 7.5 x 2.5 cms. This cellular structure had a density of 0.046 grams per cubic

centimetre, and a pore size (cell face diameter) of about 0.3 mm.; the tensile strength of this product was 35.9 pounds per square inch.

The blocks were treated with a 10%, by weight, aqueous solution of sodium hydroxide at 50°C. for varying lengths of time, and then washed with dilute acid and water and dried as described in Example 2.

Results were as follows:

Time of Treatment (min.)	Membranes Removed	Density (grams per cc.)	Weight Loss (%)	Load (psi) required to compress					
				5%	10%	20%	30%	40%	50%
0	no	0.046	0.0	1.52	1.74	1.85	1.91	1.97	—
2	partly	0.046	0.8	0.90	1.08	1.15	1.21	1.27	1.46
5	yes	0.044	3.8	0.80	0.92	0.95	0.97	1.03	1.20
10	yes	0.041	10.8	0.68	0.76	0.82	0.85	0.93	1.12
20	yes	0.036	21.2	0.46	0.58	0.62	0.64	0.70	0.85

Compression properties are measured as the pounds per square inch required to produce the given percentage compression, measured

as $100 \times (1 - \text{thickness}/\text{original thickness})$.

By comparison with the untreated cellular structure, the reticulated products free of cell

face membranes are stronger, tougher, and more cohesive. The product of the 10 minute alkali treatment is optimum in balance between completeness of membrane removal and freedom from excessive weight loss; the im-

proved physical properties of this reticulated product as compared to the original foamed cellular structure are shown in the following table:

	Density (grams per cc.)	Tensile Strength (psi)	Tensile Strength at Unit Density (psi)		
			Elongation (%)	Tear Strength (lbs/inch)	
10	Cellular Structure	0.046	35.9	780	5.2
	Reticulated Structure	0.041	36.3	885	5.4

15 Tear strength as reported above was measured on a notched sample. Manual tests on unnotched samples indicate a more sharply marked superiority of the reticulated structure in tear resistance, as a result of the combination of increased tensile strength and increased elongation.

EXAMPLE 5.

20 This example describes preparation of another polyester polyurethane foam.

The following materials are blended together at room temperature: 40 parts by weight of the polyester resin (alkyd) employed in Example 1; 0.04 parts by weight of the polyoxethylated vegetable oil employed in Example 1; 1.1 parts by weight of water, and 0.4 parts by weight of diethylethanolamine.

To the above mixture are then added 15 parts, by weight, of the mixture of toluene-2,4-diisocyanate and toluene-2,6-diisocyanate employed in Example 1.

35 The resulting combination is mixed thoroughly with rapid agitation for 20 seconds, and immediately poured into a container of sufficient volume to permit expansion, the temperature rising to about 85°C. After about 15 minutes, the container including the foamed mass is placed in an oven and maintained at 70°C. for 16 hours. The foam is then removed from the container and cut into blocks.

40 The density of the foam is 0.045 grams per cubic centimetre; the tensile strength is 2.0 kilograms per square centimetre (28.5 psi),

and the dry softness is 5 mm. The proportion of closed cells is very small, the pores having an average diameter of 0.2—0.3 mm.

EXAMPLE 6.

Blocks of open-celled polymeric polyester polyurethane sponge prepared as described in Example 5, having a tensile strength of 28.5 pounds per square inch and a density of 0.045 grams per cubic centimetre, are immersed in the following bath, maintained at 60°C., for various periods of time:

sodium hydroxide	110 parts	55
water	890 parts	

The blocks are kneaded repeatedly to ensure thorough penetration of the solution. The blocks are then removed from the bath, squeezed to remove excess solution and washed with water; then they are immersed in a 2% aqueous acetic acid solution and kneaded repeatedly to neutralize any residual sodium hydroxide. The blocks are then washed with water and dried at 120°C. for two hours.

In 10 minutes, elimination of a major portion of the cell faces is visually evident and after 15 minutes, the treatment results in the removal of substantially all of the cell faces leaving a fine three-dimensional network of the original strands defining the outlines of the original cells. A greater decrease in weight, but no loss of the reticulated structure is observed in 25 minutes treatment.

The results are as follows:

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Time of Treatment	Density (grams per cc.)	Weight Loss (%)	Softness (mm.)		Hydrophilicity (%)
			Dry	Wet	
0	0.045	0.0	5	10	10
10	0.041	16.1	12	15	90
15	0.035	20.8	12	18	87
25	0.029	34.3	17	25	84

EXAMPLE 7.

A foamed open-cell polyester polyurethane is prepared as described in Example 5. The measured tensile strength of this cellular product was 20 pounds per square inch, and the density, 0.047 grams per cubic centimetre.

Blocks of this cellular product are treated with aqueous NaOH, 110 parts, by weight, in 980 parts of water, at 60°C., as described in

Example 6, for varying lengths of time. A substantial degree of cell face removal is noted within five minutes, while the reticulated structure remains as an integral, recoverable material after treatment times up to 25 minutes and longer.

In the following table are presented results of the treatment:

Time of Treatment (min.)	Membranes Removed	Density (grams per cc.)	Weight Loss (%)	Load (psi) required to compress					
				5%	10%	20%	30%	40%	50%
0	no	0.047	0.0	0.12	0.28	0.46	0.54	0.62	0.71
5	yes	0.044	6.0	0.12	0.27	0.40	0.46	0.52	0.60
10	yes	0.040	14.1	0.11	0.20	0.28	0.33	0.39	0.46
15	yes	0.034	27.7	0.05	0.11	0.16	0.19	0.24	0.29
25	yes	0.027	41.8	0.03	0.05	0.07	0.09	0.11	0.14

The porous and soft reticulated products are of increased strength and cohesiveness as compared to the untreated cellular structure, and are markedly less easily torn. The product of 10 minutes treatment, with a 14.1% weight decrease as compared to the original foamed structure, has an elongation of 392%, as compared to 295% for the original structure, and the tensile strength of the former at unit density is 460 pounds per square inch, as compared to 425 pounds per square inch for the latter.

EXAMPLE 8.

In this example, a foamed polymeric polyester polyurethane is prepared as described in Example 1, but having pores averaging 1.5—3 mm. in diameter. Pore size is increased by addition of a small quantity of SAE motor oil to the mix prior to foaming. Blocks of the foamed cellular structure are immersed in a 10% solution of sodium hydroxide maintained at 90°C. for one minute. The blocks are repeatedly kneaded while immersed. The blocks are then removed from the bath and washed with cold water, washed with dilute acetic acid to neutralize any remaining sodium

hydroxide, and again washed with water. The blocks are then washed with sodium bicarbonate solution, and again with plain water. They are then dried in an oven at 70°C. for 3 hours.

This treatment results in removal of the original cell faces, leaving a network of the original strands. The product is somewhat more coarse than the products of the preceding examples.

With a block of foam having an original density of 0.039 grams per cubic centimetre, after treatment, the density is 0.023, and the original dry softness of 7 mm. is increased to more than 20 mm.

With a foamed product of the 1.5—3 mm. pore size having a density of 0.041 grams per cubic centimetre, the treatment produces a decrease in density to 0.036 grams per cubic centimetre, and the pressure in pounds per square inch required to produce 5% compression of the structure is reduced from 1.90 to 0.54. Improvement in the strength properties of the structure is observed as shown in the following table:

	Density (grams per cc.)	Weight Loss (%)	Tensile Strength (psi)	Tensile Strength at Unit Density		Tear Strength (lbs/inch)
				Elongation (%)		
70	Cellular Structure	0.041	0.0	24.0	585	255
	Reticulated Structure	0.036	11.4	24.2	665	385

EXAMPLE 9.

In this example a block prepared as in Example 1, but having cell faces averaging about 4 to 8 mm. in diameter, is subjected to the same treatment as in Example 8.

The treatment removes all the original cell faces, leaving a coarse network of the original strands.

From a cellular structure with an 0.058

grams per cubic centimetre density, there was produced a reticulated structure of density 0.037. The original dry softness of this foamed structure was 5 mm.; after treatment the softness is 12 mm.

In a repetition of this procedure, with a cellular structure of 4 to 8 mm. pore size and an original density of 0.044, results obtained were as follows:

	Density (grams per cc.)	Weight Loss (%)	Tensile Strength (psi)	Tensile Strength at Unit Density	Tear Strength (lbs/inch)
Cellular Structure	0.044	0.0	15.4	350	3.6
Reticulated Structure	0.041	7.4	15.8	390	6.1
Load (psi) required to compress					
	5%	10%	20%	30%	40%
Cellular Structure	1.20	1.84	1.67	1.68	1.77
Reticulated Structure	0.34	0.67	0.67	0.72	0.76
				50%	
					1.88
					0.94

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EXAMPLE 10.

This example describes steam treatment of a polyester polyurethane cellular structure to produce a reticulated structure.

Blocks of a foamed structure prepared as described in Example 1 and having a pore size of about 0.3 mm. and a tensile strength of 35.9 pounds per square inch are wet out with water, and then placed in a pressure vessel and subjected to the action of saturated steam at 20 psi gauge.

At the end of 4 hours, there is observed a decrease in density to 0.044 psi, and a weight loss of 4.7%. The product is a reticulated

structure which is markedly softer and more porous than the original cellular material.

EXAMPLE 11.

In this example, there is employed a commercial polyester polyurethane foam (sold under the registered Trade Mark "Unifoam AA" by W. T. Burnett & Co., Baltimore, Maryland).

Blocks of the foam were treated respectively for $\frac{1}{2}$ and for four minutes with 10% aqueous sodium hydroxide at 80°C., and then washed with water and dried at 100°C.

Results were as follows:

Time of Treatment (min.)	Density (grams per cc.)	Elongation (%)	Load (psi) required to compress		
			10%	50%	80%
0	0.039	220	0.73	0.98	3.45
$\frac{1}{2}$	0.038	240	0.41	0.67	2.35
4	0.028	280	0.12	0.23	1.15

50 Removal of cell faces was visually evident in the block subjected to the $\frac{1}{2}$ minute treatment, while the product of 4 minutes treatment was a fine network of strands.

EXAMPLE 12.

This example describes preparation of a polyalkylene ether polyurethane cellular structure.

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Component A.

T a closed agitated vessel equipped with a nitr gen gas sweep were charged at 40°C., 100 parts by weight of a molten polyalkylene ether, having a hydroxyl number of 37.6; water content of 0.04%; and melting point about 35°C., identified as "Teracol 30", which is believed to be a 1,4-polybutylene ether glycol (sold by E. I. duPont de Nemours & Company, Inc., Wilmington, Delaware). Next, 12.6 parts by weight of the Toluene-2,4- and 2,6-diisocyanate mixture employed in Example 1, at a temperature of 35°C., were added and agitation was commenced. There was a mildly exothermic reaction, the temperature rising to 45–50°C. Heat was then applied and the mixture was maintained at 60°C. for 2½ hours. Then an additional 12.6 parts of the diisocyanate were added and the temperature was raised and maintained at 140°C. for 2½ hours. The charge was then cooled to 50°C. and a further 3.7 parts by weight of the diisocyanate were added and mixed in. Finally, the product was allowed to cool to room temperature, 25°C.

Compound B.

A blend, at 30°C., was prepared of 51 parts by weight of dioctyl sebacate, a plasticizer-softener; 10 parts by weight of N-methylmorpholine and 2.5 parts by weight of triethylamine, catalysts; 5.0 parts, by weight, of a conventional silicone foam stabilizer, [Dow Corning DC-200 (50 cstks.)]; and 22.5 parts by weight of water.

To component B were added 1000 parts, by weight, of component A, and the mixture

was stirred rapidly for about 20 seconds. Immediately thereafter the mass was poured into a container of sufficient volume to permit expansion; after about 30 minutes the container together with the foamed mass was placed in an oven and maintained at 70°C. for 16 hours. The product in the form of an open-celled cellular structure was removed from the container and cut into blocks. Density of the blocks was about 0.031 g/cc. Pore size was about 0.1 mm. in diameter.

EXAMPLE 13.

This example describes preparation of a skeletal polymeric polyether polyurethane celliform product.

A block of the cellular polymeric polyether-polyurethane foam of Example 12 was immersed and kneaded in a bath composed of:

sodium hydroxide ... 200 parts by weight
water 800 parts by weight

at the boil temperature of the bath for a period of 10 minutes. The block was then removed, washed well with cold water, and rinsed with 2% acetic acid to neutralize any residual sodium hydroxide. Finally it was washed in water and dried at 100°C. for 3 hours.

Visual examination of the product indicated the membranes covering the cell faces had been removed leaving behind a characteristic porous skeletal structure.

Loss of weight was very small, less than 2%.

Tests on this product and on an untreated block of the Example 12 product gave the following results:

	Untreated	Treated
Tensile Strength—psi	14	20
Softness		
psi to compress 10%	0.36	0.18
psi to compress 20%	0.47	0.25
psi to compress 30%	0.51	0.30
psi to compress 50%	0.61	0.40

In addition, the high-humidity age resistance was improved by the treatment as indicated by

the following results of a 14 day exposure to 100% relative humidity at 90°C.: 75

psi to compress 25%	Untreated	Treated
Sample before ageing	0.50	0.31
Sample after ageing	0.37	0.34
psi to compress 50%		
Sample before ageing	0.64	0.45
Sample after ageing	0.52	0.47

It will be noted that while the untreated sample lost considerable load bearing capacity on ageing, the treated sample was not harmed and indeed appeared to be somewhat improved

by the ageing.

Thermal conductivity was changed very little by the treatment:

	Untreated	Treated
K—BTU/hr/ft ² /°F/inch	0.334	0.353

- 10 Manual tests indicated a marked increase in tear resistance as a result of the treatment.

EXAMPLE 14.

This example describes preparation of a polyalkylene ether-amine polyurethane cellular structure.

15 **Component A.**

To a closed vessel equipped with an agitator and a nitrogen gas sweep were charged, at an initial temperature of 25°C., 10.3 parts by weight of the above-identified mixture of 20 isomeric toluenediisocyanates, and 100 parts

by weight of a polyether-amine prepared by sequentially adding propylene and ethylene oxide to ethylene diamine, "Tetronic 701" sold by Wyandotte Chemicals Corporation, Wyandotte, Michigan). The mixture was allowed to react and the temperature was raised to 80°C., and maintained for 1 hour. Next an additional 25 parts, by weight, of the diisocyanate were added and mixed in for 1 hour at 80°C. The resulting product was then allowed to cool to room temperature.

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Component B.

The following were blended together at 25° C.:

Water	2.2 parts by weight
N-methylmorpholine	0.8 parts by weight
Triethylamine	0.2 parts by weight
Foam stabilizer of Example 12	0.5 parts by weight
This was added to 105 parts, by weight, of a mixture composed of:	
Component B	100 parts by weight
The toluenediisocyanate employed in Example 1	5 parts by weight

and mixed in rapidly for about 20 seconds. The result was then transferred to a container large enough to permit expansion. After about 30 minutes the container together with the foamed product was placed in an oven at 70° C. for 16 hours.

- 35 The resulting product was a flexible cellular mass having a density of 0.032 g/cc, and pores about 0.2 mm. in diameter. The proportion of closed cells was very small.

EXAMPLE 15.

40 This example describes preparation of a skeletal polymeric polyether-amine polyurethane product.

Blocks of the polymeric polyether-amine polyurethane cellular product of Example 14

were treated for various periods of time in boiling 20% sodium hydroxide as described above. The treated products have a major proportion, up to all, of the cell membranes eliminated, and are porous, reticulated structures. Improved strength properties are observed in the products treated for 5—15 minutes; after 20 minutes treatment, a very soft, fine reticulated structure is obtained.

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Results were as follows:

Time of Treatment (min.)	Density (grams per cc.)	Weight Loss (%)	Tensile Strength (psi)	Tensile Strength at Unit Density (psi)	Elongation (%)
0	0.032	0.0	4.8	150	105
5	0.031	3.1	6.2	200	165
10	0.030	5.7	6.5	217	165
15	0.029	10.8	6.9	238	220
20	0.023	27.9	3.1	135	170

Softness

Time of Treatment (min.)	Load (psi) required to compress—					
	5%	10%	20%	30%	40%	60%
0	0.29	0.30	0.33	0.35	0.39	0.57
5	0.15	0.19	0.20	0.21	0.24	0.36
10	0.11	0.12	0.13	0.14	0.16	0.27
15	0.07	0.08	0.09	0.10	0.12	0.19
20	—	0.01	0.02	0.03	0.04	0.06

EXAMPLE 16.

This example describes steam hydrolysis of a cellular structure.

Blocks of polyether-polyurethane cellular product prepared as in Example 12 were

autoclaved with 20 psig steam for various periods of time. The blocks were then dried at 105°C. for 3 hours and examined.

Results were as follows:

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Time of Treatment—hr.	Wt. Loss %	Tensile Strength (psi)	Elongation (%)	Tear Strength lbs/inch
0	0.0	14.1	178	1.94
2	0.8	22.9	318	2.81
4	0.7	31.0	365	4.5
8	0.9	19.4	415	5.5

Time of Treatment—hr.	Load (psi) required to compress					
	5%	10%	20%	30%	40%	50%
0	0.18	0.40	0.55	0.59	0.64	0.70
2	0.14	0.26	0.35	0.40	0.45	0.52
4	0.12	0.20	0.26	0.29	0.33	0.39
8	0.10	0.17	0.24	0.28	0.32	0.39

Visual examination indicated that the 2 hour treatment resulted in incomplete removal of the cell face membranes, while the 4 and 8 hour treatments resulted in substantially complete removal of all the membranes.

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EXAMPLE 17.

Blocks of polyether-amine polyurethane

Time of Treatment—hr.	Wt. Loss %	Tensile Strength (psi)	Elongation (%)	Tear Strength Lbs/inch
0	0.0	5.2	100	1.23
1	1.9	6.8	116	0.78
2	2.4	5.3	118	0.88
4	4.5	5.9	130	—
8	6.5	5.6	130	0.79

Time of Treatment—hr.	Load (psi) required to compress—					
	5%	10%	20%	30%	40%	50%
0	0.28	0.29	0.31	0.35	0.38	0.45
1	0.15	0.19	0.21	0.25	0.27	0.32
2	0.13	0.19	0.20	0.23	0.26	0.31
4	0.12	0.13	0.13	0.14	0.15	0.18
8	0.11	0.13	0.13	0.14	0.16	0.18

Visual examination indicated that the cell face membranes were substantially completely removed from all the treated samples.

EXAMPLE 18.

This example describes acid hydrolysis of a cellular product to produce a reticulated structure.

Blocks of polyether-polyurethane cellular product prepared as in Example 12 were

kneaded in 19% hydrochloric acid solution at a temperature of 50°C. for 15 and for 60 minutes, respectively. The blocks were then washed well with water, dried at 105°C. for

25

3 hours and examined. Visual examination indicated that both treated samples had substantially all the cell face membranes removed. Weight loss was low, 0.4—0.5%. Results were as follows:

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Time of Treatment—Min.	Load (psi) required to compress—					
	5%	10%	20%	30%	40%	50%
0	0.21	0.42	0.53	0.58	0.62	0.68
15	0.14	0.26	0.37	0.41	0.45	0.52
60	0.16	0.27	0.37	0.42	0.47	0.54

EXAMPLE 19.

In this example a block prepared as in Example 1 and having the same dimensions is immersed in a bath at 24°C., composed of:

38% aqueous hydrochloric acid

water 500 parts by weight

The block is kneaded repeatedly after 40

immersion to ensure thorough impregnation thereof by the solution. The block is left in the bath for 1½ hours. The block is then removed from the bath, washed well with cold water and dried at 120°C. for two hours.

5 The results are as follows: The dry softness is 19 mm., the wet softness is 22 mm., the hydrophilicity is 17% and there is no appreciable weight loss.

10 EXAMPLE 20.

In this example a block prepared as in Example 1 and having the same dimensions is immersed in a bath maintained at 90°C., having the composition:

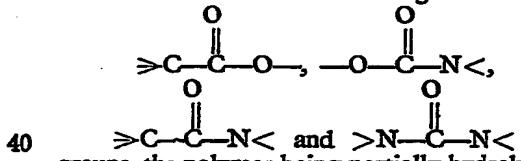
15 trisodium phosphate ... 100 parts by weight
(crystalline, reagent grade)
water 900 parts by weight

The block is kneaded repeatedly after immersion to ensure thorough penetration of the solution. After 10 minutes of immersion, the block is removed from the bath, washed with water and dried at 120°C. for two hours.

20 The results are as follows: Dry softness is 19 mm., wet softness is 20 mm., hydrophilicity is 76% and there is no appreciable weight loss.

WHAT WE CLAIM IS:—

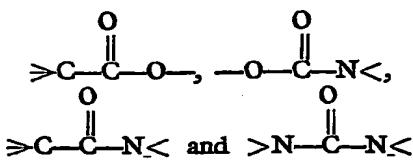
1. A foamed, open-cell cellular polymeric 30 polyurethane material of the form of an integrally formed 3-dimensionally reticulated structure comprising a network of strands defining the outlines of a plurality of polygons making up a plurality of polyhedrons, at least 35 a major portion of the faces of the polyhedrons being open, in which at least a portion of the linking groups in the polymer chain are selected from the class consisting of



40 groups, the polymer being partially hydrolyzed.

2. A material according to claim 1, in which the external and internal surfaces of the material are partially hydrolyzed.

45 3. A method of modifying the physical properties of a foamed, open-cell, cellular structure composed of polymeric polyurethane material in which at least a portion of the linking groups in the polymer chain are selected from the class consisting of



groups, which comprises subjecting said structure to the action of a hydrolyzing agent under hydrolyzing conditions for a time sufficient to alter the physical characteristics of said cellular structure.

4. A method according to claim 3, in which the hydrolysis is carried out until a portion of the cell faces have been eliminated and there is a weight loss of from about 5% to 15% of the original mass, the hydrolysis being arrested before complete destruction of the cellular structure.

5. A method according to claim 3, in which the hydrolysis is carried out until at least a major portion of the cell faces have been eliminated, and the hydrolysis is arrested to recover a 3-dimensionally reticulated network of interconnected strands.

6. A method according to any one of claims 3 to 5, in which the polymer is an isocyanate-derived polymer.

7. A method according to any one of claims 3 to 5, in which the polymer is a polymerized polyester polyurethane.

8. A method according to any one of claims 3 to 5, in which the polymer is a polymerized polyether polyurethane.

9. A method according to any one of claims 3 to 8, in which the hydrolyzing agent is aqueous alkali.

10. A foamed, open-cell, cellular polyurethane polymeric material substantially as hereinbefore described and as illustrated in the accompanying drawings, with respect to Example 2—4, 6—11, 13, and 15—20.

11. A method of modifying the physical properties of a foamed, open-cell, cellular structure substantially as hereinbefore described and as illustrated in the accompanying drawings.

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Agents for the Applicants.

Reference has been directed, in pursuance of Section 8 of the Patents Act, 1949, to Specification No. 789,481.

858,127

1 SHEET

COMPLETE SPECIFICATION

This drawing is a reproduction of
the Original on a reduced scale.

FIG.1

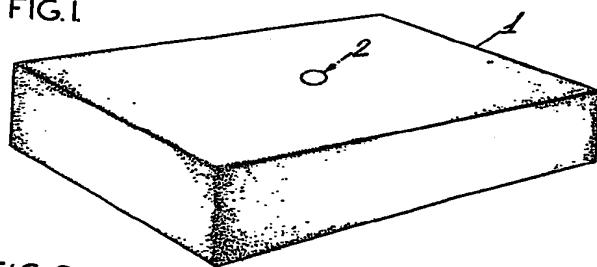


FIG.2.

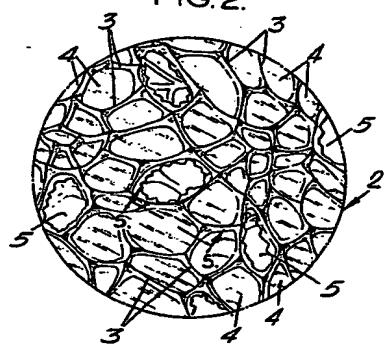


FIG.3.

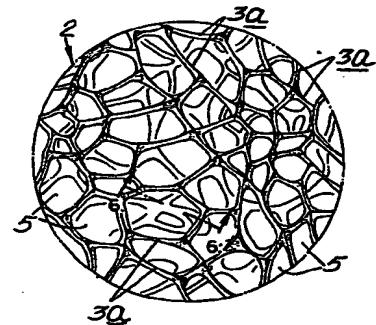


FIG.5.

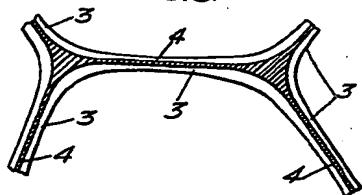


FIG.6.

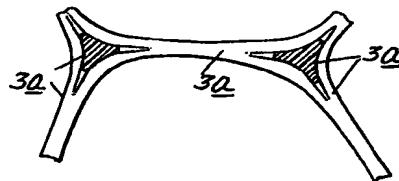


FIG.4.

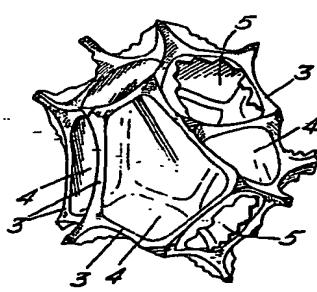


FIG.7.

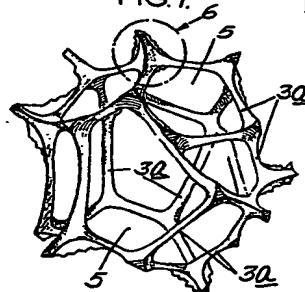


FIG.8.

